

Synthesis and Properties of Styrene–Butylacrylate Emulsion Copolymers Modified by Silane Compounds

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ABSTRACT: Styrene (St)/butyl acrylate (BA) copolymers were prepared by adding triethoxyvinylsilane (TEVS), trimethoxyvinylsilane (TMVS), and triphenylvinylsilane (TPVS), each one through emulsion copolymerization. The polymerization was performed with methacrylic acid and auxiliary agents at 80°C in the presence of potassium peroxydisulfate as the initiator. Nonylphenol ethylene oxide-40 units (NP-40) and sodium lauryl sulfoacetate were used as nonionic and anionic emulsifiers, respectively. The resulting copolymers were characterized by using Fourier transform infrared spectroscopy. Thermal properties of the copolymers were studied by using thermogravimetric analysis and differential scanning calorimetry. The morphology of copolymers was also investigated by optical

microscopy, and then the effects of silicone kinds and concentrations on the properties of the St/BA emulsion copolymers were discussed. The obtained copolymers have high solid content (50 %) and can be used in emulsion paints as a binder. The comparison of three different vinyl silanes indicates that the TEVS influences on the copolymer properties more than the others. The calculations of monomer conversion and monomer conversion versus time histories indicate that by increasing the silicone concentration, the polymerization rate decreases. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1037–1044, 2009

Key words: emulsion polymerization; silicones; thermal properties

INTRODUCTION

Copolymers of acrylics and styrene (St) have many specific features such as good film-forming, gloss, transparency, mechanical properties, and their corresponding products have been widely used as coatings, paints, and adhesives. However, the poor ultraviolet light resistance and low (or high) temperature resistance limit their applications. In contrast, silicone compounds have many excellent properties such as high flexibility and hydrophobicity, low surface tension, low glass transition temperature (T_g), weather resistance, and excellent thermal stability. However, the low tensile strength and relative high costs limit their applications. Thus, the combination of polyacrylates or poly(acrylates-co-styrene) with silicone has been of importance and interest during the past few decades.^{1–22} As waterborne paint is environmentally friendly, latices have been the most popular products for coatings. Modification of polyacrylates or poly(acrylates-co-styrene) latices by silicone is a convenient and effective way for improving their properties, that is why there is abundant literature about this study, and because of

the strong commercial interest a number of works have been appeared as patents.^{1–6,10–16} Among these works, three methods were widely used: (a) core-shell (polysiloxane-other polymers) composite latex particles were generally prepared by multistage emulsion polymerization typically involving, first, forming the polysiloxane seed particle and, second, polymerizing the second monomers into the polysiloxane seed^{1–9}; (b) copolymerization of vinyl monomers with vinyl silanes or polymerizable polysiloxanes were also investigated^{10–18}; and (c) in recent years, novel core/shell latex particles with polyacrylates or polystyrene as a core and with polysiloxane as a shell were successfully synthesized through a special seeded emulsion polymerization, and the properties of the latices and latex films were also studied.^{19–23}

In this work, the polymer latexes were successfully prepared by the emulsion copolymerization of St/butyl acrylate (BA) monomers catalyzed by NP-40 and sodium lauryl sulfoacetate (SLSA). By changing the silicone kinds and concentrations, a series of the latexes with different silicone content were obtained. The morphology of the latex was observed by optical microscopy (OM). The copolymerization between St/BA monomers and silicones was confirmed by the Fourier transform infrared spectroscopy (FTIR). The heat stability, T_g , and water absorption ratio were also investigated.

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TABLE I
Polymerization Recipe at 80°C

Compound	Initial charge	Feed	Total
St (g)	6	44	50
<i>n</i> -BA (g)	7	45	52
MAA (g)	0.05	0.45	0.50
Silicone (g)	10 wt %	90 wt %	Variable (0–12)
Buffer: sodium pyrophosphate (g)	0.30	–	0.30
Initiator: K ₂ S ₂ O ₈ (g)	0.06	0.34	0.40
Demineralized water (g)	54	42	96
Nonionic emulsifier: Nonylphenol ethylene oxide-40 units (NP-40) (g)	2.80	0.60	3.40
Anionic emulsifier: Sodium lauryl sulfoacetate (SLSA) (g)	–	3.0	3.0

EXPERIMENTAL

Materials

The monomers St (Aldrich) and BA (Aldrich) were freed from the inhibitor by shaking with 10% aqueous NaOH, washing with distilled water and drying over Na₂SO₄. They were then distilled under reduced pressure before use and stored at –20°C to avoid thermal polymerization. The methacrylic acid (MAA; Merck) was distilled directly under vacuum and stored at 0°C. Triethoxyvinylsilane (TEVS; Merck), trimethoxyvinylsilane (TMVS; Merck), and triphenylvinylsilane (TPVS; Aldrich) were analytically graded and used directly without further purification. The initiator potassium peroxydisulfate (KPS; Merck) and buffer, tetra-sodium pyrophosphate anhydrous (TSPP; Fluka), were used as received. The emulsifiers, SLSA and nonylphenol ethylene oxide-40 units (NP, Iconol NP-40; BASF, Germany), were also used as received. The solvents, toluene, benzene, acetic acid, xylene, *N,N'*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), *N*-methylpyrrolidone (NMP), acetone, and dichloroethane were purchased from Merck and were distilled before use. Water was distilled and deionized.

Polymerization procedure

Semicontinuous emulsion copolymerization was carried out using a 500-mL five-necked round-bottomed flask equipped with a reflux condenser, stainless steel stirrer, sampling device, and two separate feed streams. The first feed stream was a solution of BA, St, MAA, silicone, and anionic surfactant. The other feed was the initiator solution 7.8×10^{-3} mol/L. Before emulsion copolymerization startup, the reaction vessel was first charged with the desired amounts of water, SLSA as emulsifier, TSPP, and initiator solution, in this order. During polymerization, the reaction mixture was stirred at a rate of 50 rpm, and the temperature was maintained at 63°C. After 5 min, a 10% of total amount of the monomer mixture

was added to the flask in a period of 13 min. Then, the stirring rate was kept at 300 rpm and the temperature at 80°C until the end of polymerization, which was around 3 h. The polymerization was performed with a feeding rate of 1.0 mL/min under atmospheric conditions to investigate the effect of silicone kinds and concentrations on monomer conversion. A typical recipe for the preparation of a 50% solid product is given in Table I. To determine the conversion percentage during the polymerization process, it was necessary to withdraw samples at 15-min intervals from the reaction vessel. These samples are relatively small so that the overall composition in the reactor is not seriously affected; once a sample is removed and put in a watch glass, polymerization is terminated by the addition of 7 ppm hydroquinone. Then, two drops of ethanol are added to the sample as a coagulant, and the contents of the watch glass were evaporated at room temperature and then dried to a constant weight in a vacuum oven. The conversion % was determined gravimetrically. The purification and precipitation of the polymer were done using Grassie's method.²⁴ However, the produced copolymers have low solubility in various solvents such as toluene, benzene, acetic acid, xylene, DMF, DMSO, NMP, acetone, and dichloroethane, which makes it difficult for their characterization by GPC or NMR. Their morphology as well as thermal properties gave important information about their structure and property relation. The appearance properties of the products, such as adhesiveness, transparency of the film, and elasticity, are excellent and indicate the formation of copolymers. The reproducibility of the monomer conversion was checked by repeating the experiments, and each monomer conversion considered in this article is an average of at least four measurements. The deviations between four runs was always less than 3%.

Polymer characterization

Differential scanning calorimetry (DSC) thermograms were taken on a Mettler TA 4000 Model

apparatus at a heating rate of 10°C/min. The T_g was taken at the onset of the corresponding heat capacity jump. Thermogravimetric analysis (TGA) measurements of copolymers were carried out by a Dupont TGA 951 under nitrogen atmosphere at a heating rate of 10°C/min. FTIR spectra of the copolymers were taken using a Nicolet Impact 400 D Model spectrophotometer, and saturated water absorption (A_w) of the films was measured as follows: about 2 g of film was put into water for 14 days at 20°C, and then it was dried again. By comparing the weight of the film before drying (W_1) and after drying (W_2), the absorption ratio can be calculated by A_w (%) = $((W_1 - W_2)/W_2) \times 100$.

RESULTS AND DISCUSSION

The effect of silicone types and its concentration

The addition of silicone compounds in acrylic emulsion provides beneficial effects by improving various mechanical properties such as water and weather resistances and good acid and alkali resistance.^{25–32} In addition, the incorporation of silicone plays the roles of coupling agent and softener³³ and it is enriched on surface of the film.³⁴ On the other hand, You et al.³⁵ demonstrated that silanes can be bonded with hydroxyl groups on the surface of substrate to increase the adhesion, and FTIR analysis also indicated that organic functional silanes can be polymerized with other monomers.

Although copolymerization of St and BA has been well established,^{36–65} their copolymerization in the presence of TMVS, TEVS, and TPVS has not been reported. Therefore, the roles of these monomers are not perfectly clear. It is possible that during copolymerization process, these monomers will make part of the copolymer chain. However, the extents of their incorporation in the polymer chain were not

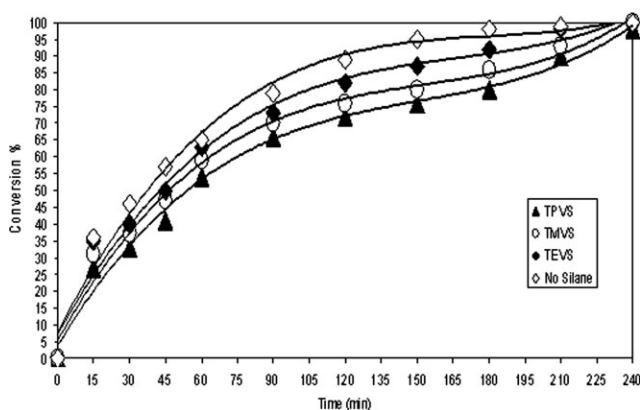


Figure 1 The effect of silicone types on monomer conversion versus time at (▲) TPVS; (○) TMVS; (◆) TEVS; and (◇) without silane; $[M]_0 = 4.60$ mol/L, $T = 80^\circ\text{C}$, 300 rpm, $[I]_0 = 7.8 \times 10^{-3}$ mol/L.

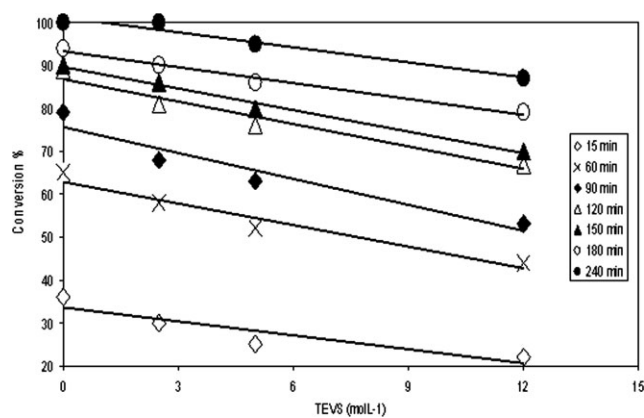


Figure 2 The effect of initial TEVS concentration on monomer conversion versus silicone percent at (◇) 15; (×) 60; (◆) 90; (△) 120; (▲) 150; (○) 180; and (●) 240 min. $[M]_0 = 4.60$ mol/L, $[TEVS] = 0.30$ mol/L, $T = 80^\circ\text{C}$, 300 rpm, $[I]_0 = 7.8 \times 10^{-3}$ mol/L.

measured. Figure 1 shows the effect of silicone types on the monomer conversion versus time, and Figure 2 shows the effect of TEVS concentration on the monomer conversion versus TEVS concentration, respectively, where the initial initiator and total monomer concentrations were fixed at $I_0 = 7.8 \times 10^{-3}$ mol/L and $[M]_0 = 4.60$ mol/L. These figures show that the rate of reaction changes with the silicone types, and according to Figure 1, the reaction rate decreases from St/BA to TPVS containing St/BA copolymers and the maximum rate is obtained by St/BA copolymers. Figure 2 shows that the reaction rate of St/BA copolymers is decreased by increasing TEVS and the same results were obtained for the other silane compounds. It is known that the rates of propagation and consequently copolymerization in a radical copolymerization reaction are inversely related to the termination rate constant. As the amount of silicone increased, it acted as a chain transfer agent and the rate of polymerization decreased. Although chain transfer generally does not decrease the polymerization rate, this matter has been observed by the authors for many times and it can be justified as follows: The radicals obtained from vinyl silanes are more stable in comparison with other radicals, which exist in the silanes containing emulsion copolymers. This stability is due to the π -bonds and resonance effects of double bonds, and consequently a reduction in the reaction rate was observed.

Among these silane compounds, TEVS has the best result and it is a suitable comonomer for modification of St/BA emulsion copolymers. Although these silane compounds have the same vinyl groups, their other substituents are different. For this reason, the steric hindrance and electronic influences of these groups are not the same, and therefore the

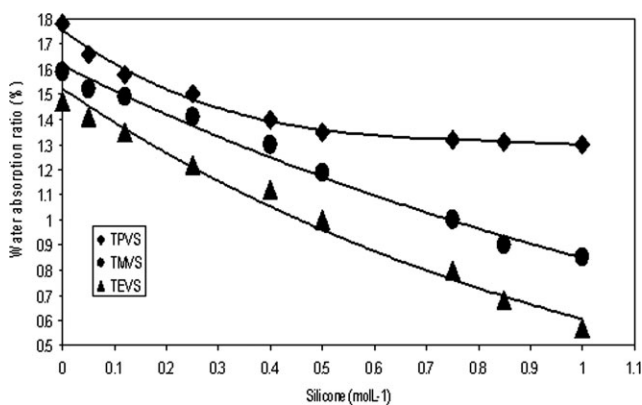


Figure 3 The effects of the silicone content seed latex to water absorption ratio of the latex films at (◆) TPVS; (●) TMVS; and (▲) TEVS. $[M]_0 = 4.60$ mol/L, $T = 80^\circ\text{C}$, 300 rpm, $[I]_0 = 7.8 \times 10^{-3}$ mol/L.

reactivity of the corresponding silane groups in St/BA emulsion copolymers does not show the same effect. In TPVS, the phenyl groups are sterically hindered and increased the bulkiness around the center of the reactions. On the other hand, phenyl is an electron-withdrawing group and therefore destabilized the reaction. The overall effect of phenyl groups is to decrease the rate of reactions. In the case of TEVS and TMVS, the alkoxy groups are electron donating and can stabilize the intermediate in the reactions, and consequently the rate of reaction increased.

Water absorption ratio of the latex films

The poly-St/BA latex was one of the basic formulation components of the waterborne coatings, and the water resistance of the waterborne coatings was mostly determined by the latex hydrophobicity. The water absorption ratio of the latex films is an important parameter for characterization of the hydrophobicity. As shown in Figure 3, the absorption ratio was greatly influenced by the content of the silicone, and this influence is the same for the three different types of silicone that has been used in this study. With the increase of the silicone content, the water absorption ratio of the latex films decreased, which can contribute to the excellent hydrophobicity of silicone. So, it can be concluded that higher silicone content would give better water resistance.

Solubility and FTIR analysis

The emulsion copolymers basically have low solubility or do not have any solubility in the organic solvents. These copolymers, which have been synthesized from St, BA, and MAA with or without sili-

cone, are not exceptions. They are not soluble even in aprotic polar solvents such as NMP, DMSO, DMF, or dimethyl acetamide (DMAc). This insolubility could be due to the conversion of the polymer samples to gelation immediately during of drying under atmospheric conditions or vacuum. Different procedures for the preparation, purification, and drying of the polymer samples were carried out. For example, the product was isolated by filtration after precipitation with a large amount of methanol and dried under vacuum at 60°C . After 48 h, it was observed that it is insoluble in all of the aforementioned solvents. It is worth to mention that the obtained copolymers will turn to gel by adding two drops of ethanol after dissolving in the DMF, DMSO, THF, toluene, and benzene. The characterization of these copolymers is difficult because of their solubility. For example, NMR study of these copolymers is nearly impossible to perform, but FTIR spectra in the region from 4000 to 500 cm^{-1} were recorded with a sample prepared by making a film of the latex on the surface of a glass and drying it, and then removing the film from the glass. Figure 4 shows the typical FTIR spectra of (A) St/BA copolymers with the following silane compounds: (B) TMVS, (C) TEVS, and (D) TPVS, respectively. The peaks at 3070 , 1733 , and 1600 cm^{-1} were associated with C—H of Ph, C=O and C=C of Ph stretch of the poly(St-co-BA), respectively. Silicone could be characterized by Si—CH₃ symmetric deformation, stretching vibration at 1260 and 801 cm^{-1} , respectively; Si—O—Si asymmetric stretching in the range 1100 – 1000 cm^{-1} . From these spectra, it is clear that silicone had been successfully copolymerized to poly(St-co-BA).

Morphologies of latex particles at different silicone types

The particle morphologies of the silicone containing St/BA copolymers were examined by OM. Figure 5(A–D) is a micrograph of the latex particles of samples without adding silane, with TMVS, TEVS, and TPVS, respectively. According to these micrographs, the St/BA copolymers have a low particle size when compared with silicone-modified samples, and by increasing the silicone concentration, the particle size increases and their size distributions get narrower, and it clearly shows that the morphology of latexes are dependent on the silicone types. It is worth mentioning that the St/BA copolymers have a number of porosities on their surfaces when compared with silicone-modified sample, and by increasing the silicone concentration, the porosity decreased and reached the minimum, and the surface of polymer films were also soft and smooth. On the other hand, there are some tiny cracks on the surface of

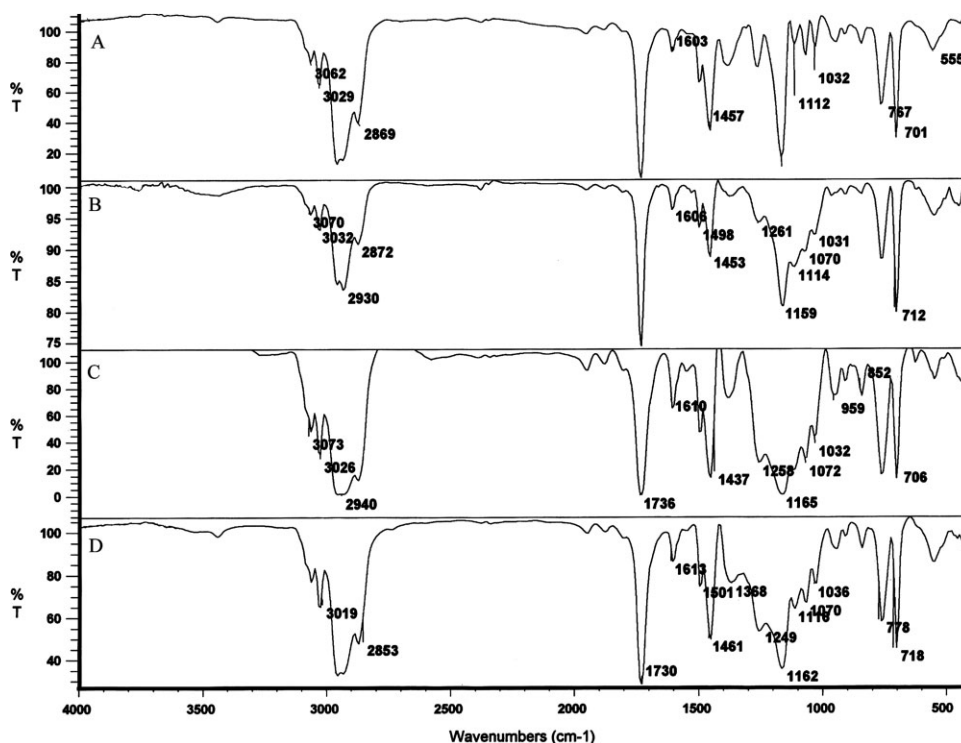


Figure 4 FTIR spectra of (A) St/BA copolymers with (B) TMVS; (C) TEVS; and (D) TPVS. $[M]_0 = 4.60 \text{ mol/L}$, $T = 80^\circ\text{C}$, 300 rpm, $[I]_0 = 7.8 \times 10^{-3} \text{ mol/L}$.

micrograph A in comparison with others. These results suggest that St/BA and MAA monomers were completely polymerized in the presence of sili-

cone, and TEVS-containing St/BA copolymer shows that the particle size distribution is uniform through the picture.

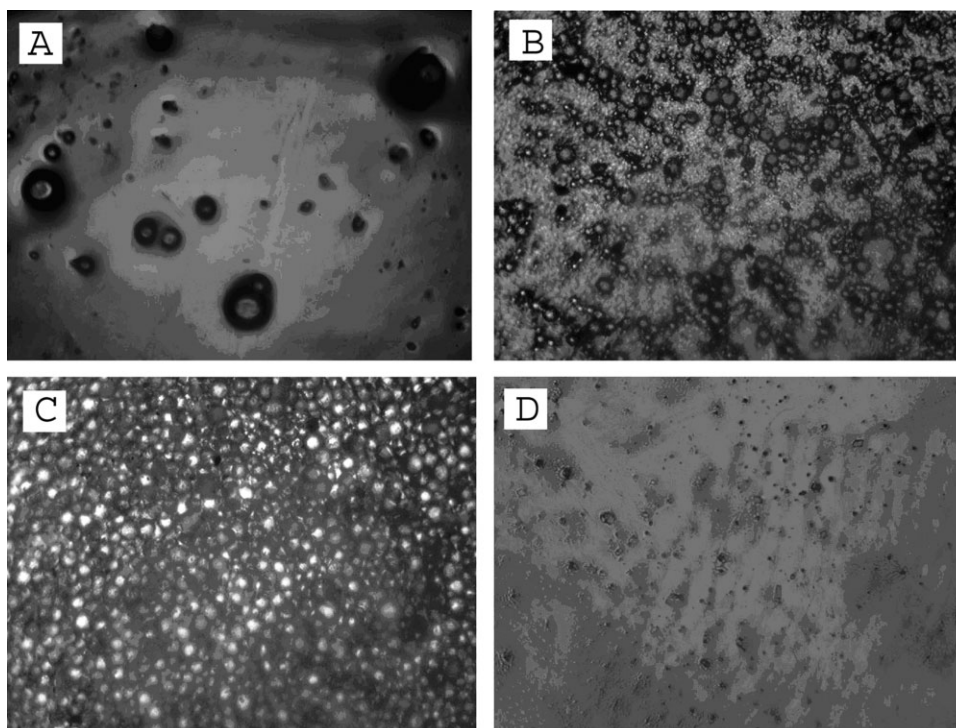


Figure 5 Optical microscopy pictures of (A) St/BA copolymer with (B) TMVS; (C) TEVS; and (D) TPVS. $[M]_0 = 4.60 \text{ mol/L}$, $T = 80^\circ\text{C}$, 300 rpm, $[I]_0 = 7.8 \times 10^{-3} \text{ mol/L}$.

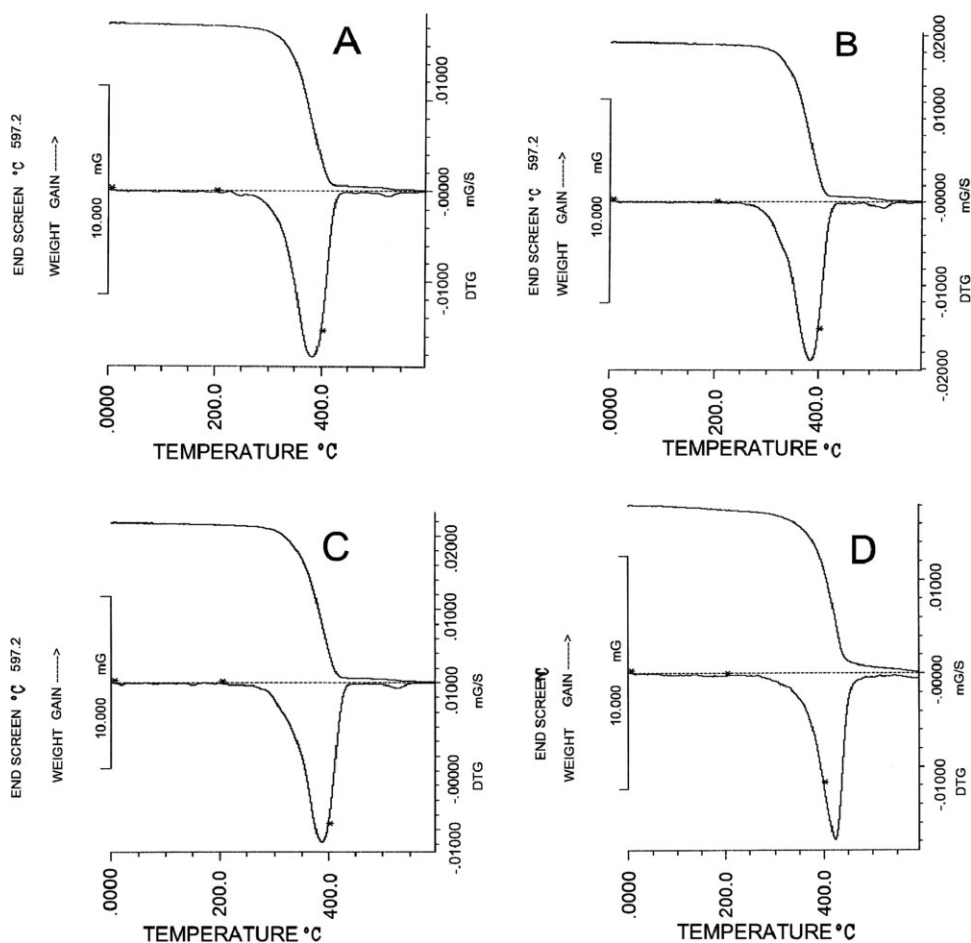


Figure 6 TGA/DTG thermograms of (A) St/BA copolymer with (B) TMVS; (C) TPVS; and (D) TEVS in N_2 atmosphere. $[M]_0 = 4.60$ mol/L, $T = 80^\circ\text{C}$, 300 rpm, $[I]_0 = 7.8 \times 10^{-3}$ mol/L.

Thermal properties

The thermal properties of St/BA and silicone-containing St/BA copolymers were evaluated by means of TGA/DTG and DSC under nitrogen atmosphere, as shown in Figures 6–8. The St/BA emulsion [Fig. 6(A)] shows a stable situation up to 200°C . The chemical decomposition will start after this temperature, and the maximum decomposition is around 380°C . On the other hand, the silicone-modified St/BA copolymers exhibited thermal decomposition, similar to the earlier one, but the maximum decomposition was around 390 , 400 , and 425°C for B, C, and D thermograms, which contain TMVS, TPVS, and TEVS, respectively. According to these results, it is concluded that the existence of silicone moiety in the copolymers causes some thermal stability, and by increasing the amount of silicone the thermal stability increases. Also, St/BA copolymers that contain TEVS has higher thermal stability than others. DSC curve of the copolymers is shown in Figure 7(A–D) for St/BA copolymers without adding silane, with TEVS, TPVS, and TMVS, respectively. Figure 7(A) reveals an endothermic shift

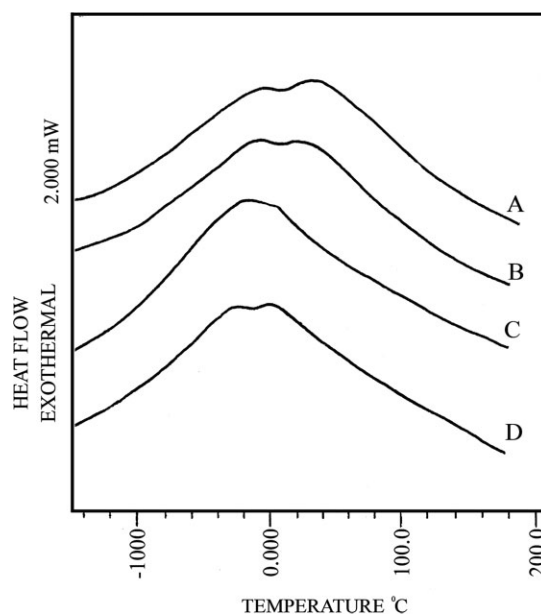


Figure 7 DSC thermograms of (A) St/BA copolymer with (B) TEVS; (C) TPVS; and (D) TMVS. $[M]_0 = 4.60$ mol/L, $T = 80^\circ\text{C}$, 300 rpm, $[I]_0 = 7.8 \times 10^{-3}$ mol/L.

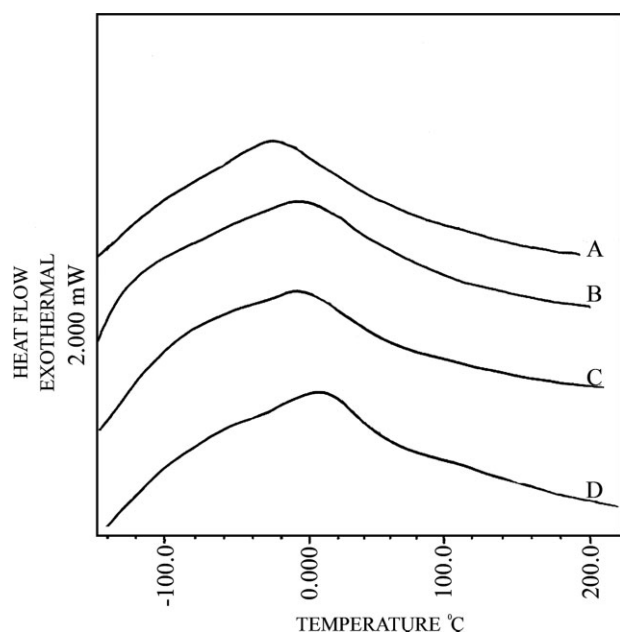


Figure 8 DSC thermograms of (A) St/BA copolymer with 24, (B) 10, (C) 2.5, and (D) 0.00% TEVS. $[M]_0 = 4.60 \text{ mol/L}$, $T = 80^\circ\text{C}$, 300 rpm, $[I]_0 = 7.8 \times 10^{-3} \text{ mol/L}$.

around 5°C , which corresponds to T_g without silicone, and the T_g is around 3°C for (B), 0 and -10°C for (C) and (D) thermograms, respectively. Figure 8(A–D) is an example of St/BA copolymers containing 24, 10, 2.5, and 0.00% TEVS-containing thermograms, respectively. Figure 8(A) reveals an endothermic shift around -20°C , which corresponds to T_g with 24% TEVS, and the T_g is around 0°C for (B), 3 and 5°C for (C) and (D) thermograms, respectively. By increasing the amount of TEVS, the T_g decreased drastically. From these data, it is interesting to mention that without silicone the resulting copolymer is thermoplastic, whereas by the addition of silicone, the copolymer will have a drastic lowering in its T_g and shifts to the elastomeric materials, while its T_m remain unchanged. According to these results, it is found that the presence of silicone moiety causes the change in thermal behavior and particularly affects the T_g .

CONCLUSIONS

Continuous emulsion copolymerization of silicone-modified St/BA emulsions initiated by KPS was evaluated. The effects of silicone kinds and concentrations on the properties of the copolymers were discussed. The following results were obtained:

1. An increase in silicone concentration caused an increase in heat stability, while the T_g and polymerization rate decreased.
2. The presence of silicone moiety in the copolymers caused conversion of thermoplastic structure to elastomeric property.

3. The obtained copolymers had good storage stability.
4. The reaction between polymerizable silicone and styrene or butyl acrylate was confirmed by FT-IR spectra.
5. The water absorption ratio of the latex films got a minimum value at latex content of 10 %.
6. The transparency of the films reduced as the silicone concentration increased
7. The TEVS has presented the best results and it is very suitable for modification St/BA emulsion copolymers.
8. The morphology of the latexes is dependent on the silicone types.

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